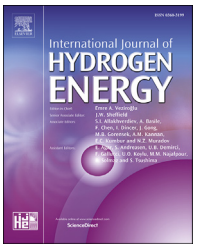
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–10

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Molybdenum oxide and molybdenum carbide coated carbon black as an electrocatalyst for hydrogen evolution reaction in acidic media

*Yan Zhang, Jianbing Zang, Chan Han, Shaopei Jia, Pengfei Tian, Hongwei Gao, Yanhui Wang**

State Key Laboratory of Metastable Materials Science and Technology, School of Materials Science and Engineering, Yanshan University, Qinhuangdao 066004, PR China

ARTICLE INFO

Article history:
Received 16 June 2017
Received in revised form
9 September 2017
Accepted 14 September 2017
Available online xxx

Keywords:
Hydrogen evolution reaction
Molybdenum oxide
Molybdenum carbide
Non-noble metal electrocatalyst

ABSTRACT

Molybdenum oxide and molybdenum carbide coated carbon black (MoO_2–Mo_2C/C) non-noble metal hybrid electrocatalyst for hydrogen evolution reaction (HER) was synthesized from a mixture of metal molybdenum (Mo) powders and carbon black particles by a spark plasma coating (SPC) method. After the SPC process, the MoO_2–Mo_2C coating can anchor strongly on carbon black with the help of intermediate products Mo_2C. The MoO_2–Mo_2C/C electrocatalyst exhibited a good HER performance with an onset overpotential of −121 mV, a high exchange current density of 6.8×10^{-2} mA cm^{-2} and a Tafel slope of −69 mV dec^{-1} in 0.5 M H_2SO_4 solution. In addition, the MoO_2–Mo_2C/C showed much higher stability than Pt/C (20 wt% Pt supported on Vulcan XC-72 carbon black) after 3000 cycles of accelerated durability tests. The enhanced electrocatalytic activity and stability of MoO_2–Mo_2C/C electrocatalyst toward HER may originate from the Mo_2C active sites formed in the process of SPC, and the effectively anchoring effect of MoO_2–Mo_2C coating on carbon black.

Introduction

In recent decades, the development of renewable energy sources has attracted great attention. Among various kinds of energy systems, hydrogen is considered as a promising energy carrier to replace fossil fuels due to its high energy density and almost no pollution to the environment [1,2]. As we know, water electrolysis has been proposed as a major route [3,4] that aims for hydrogen production and hydrogen evolution reaction (HER) is a fundamental step of water electrolysis [5,6]. Up to now, platinum (Pt)-based noble catalysts are known as the most efficient electrocatalysts for HER [7,8]. Unfortunately, the high price and shortage resource of Pt have greatly limited its performance and large scale application [9,10]. For these reasons, low cost and efficient electrocatalysts for HER should be developed to overcome this bottleneck and meet the demands for commercial application.

Recently, transition metal carbides have been regarded as effective candidate electrocatalysts for replacing Pt noble metals in HER due to their Pt-like electronic structure [11–13]. Among them, molybdenum carbide (Mo_2C) is a very promising HER catalyst in both acidic and basic media because of its unique physical and chemical properties [14,15]. However, the inherent poor electrical conductivity of Mo_2C limits its catalytic performance and commercial application [16,17]. Fortunately, the HER performance of Mo_2C can be enhanced by

* *Corresponding author.*
E-mail address: diamond_wangyanhui@163.com (Y. Wang).

https://doi.org/10.1016/j.ijhydene.2017.09.077

introducing carbon materials because of their high electrical conductivity and large surface area [18,19]. Up to now, Mo_2C nanomaterials are supported on various carbon materials including porous carbon, graphene, and carbon nanotubes [19–21] to inhibit the aggregation of Mo_2C nanoparticles, bringing out more reactive sites on the surface [22]. For instance, Chen et al. reported Mo_2C anchored to XC-72R carbon black by in situ carburization of ammonium molybdate and XC-72R carbon black under Ar flow, which revealed small onset overpotential and high exchange current density [23]. Zhang et al. synthesized a hybrid of molybdenum carbide and N-doped carbon nanotubes, exhibiting outstanding HER electrocatalytic activity and stability in acidic media [24].

It is known that metal carbides can be prepared through chemical vapor deposition (CVD) [25] or pyrolysis of metal complexes [24]. Especially, CVD is one of representative methods, in which Mo-containing gaseous reagents and carbonaceous gases are used. Nonetheless, the carbides prepared by CVD are usually contaminated with chars, which are formed during the pyrolysis process of carbonaceous gases [23,26]. Herein, molybdenum coated carbon black (MoO_2–Mo_2C/C) was designed as a highly efficient non-noble metal hybrid catalyst for HER by applying the spark plasma coating (SPC) method without using any gaseous carbon source. Instead of sintering bulk materials, spark plasma sintering (SPS) with the characteristic of rapid heating was used to coat loosely packed powders by controlling the ratio of Mo powders and carbon blacks. During the SPC process, mixed powders were rapidly heated without sintering, in which metal Mo was activated and reacted with carbon blacks to form Mo_2C. When compared with CVD method, the Mo_2C formed on carbon black prepared by SPC method can be easily separated from Mo powders by an alcohol precipitation method. Furthermore, compared with conventional vacuum coating method, the SPC method relies on rapid electro-discharge treatment which has a lower synthesis reaction temperature and shorter time [26,27].

Experimental section

Materials

Vulcan XC-72 carbon black consisting of particles of about 50 nm in diameter was supplied by Cabot Corporation. Platinum precursor ($H_2PtCl_6 \cdot 6H_2O$), concentrated sulfuric acid (H_2SO_4), N, N-dimethylformamide (DMF), acetone, ethanol and Mo powders (250 μm) were provided by Shanghai Chemical Products Ltd. Deionized water and high-purity nitrogen gas (99.9%) were used throughout the experiments.

Preparation of MoO_2–Mo_2C/C electrocatalyst

The preparation process of MoO_2–Mo_2C/C is illustrated in Fig. 1. Carbon black nanoparticles reacted with a strong carbide-forming element Mo by heating a mixture of carbon black and Mo powders by SPC. When the mixture was heated under a vacuum atmosphere, MoO_2 and Mo_2C were formed on the surface of carbon black.

MoO_2–Mo_2C/C non-noble metal hybrid electrocatalyst was synthesized by the SPC method as follows: 50 mg carbon blacks and 2 g Mo powders (m/m = 1:40) were mixed uniformly by ethanol, then poured into a graphite die (inner diameter: 30 mm). Afterwards, the graphite die was put into a spark plasma sintering apparatus (SPS-3.20 MK-IV Sodick Co. Ltd, Japan) and heated to 870 °C for 40 min in Fig. 2. During the sintering process, a hydrostatic pressure of 30 MPa and a fixed pulse pattern 12:2 ms were used. After sintering, the SPS system was cooled to 100 °C using nitrogen purging with cooling rate of about 150 °C min^{-1}. In our work, the SPS technique was used as a method for coating fabrication by using appropriate proportion of raw material, rather than as a rapid sintering technique [28]. It should be noted that excess Mo powders in the graphite die resulted in block sintering (Fig. S1), while little Mo powders led to uneven coating. By using the alcohol precipitation method the as-obtained mixture was separated into two phases: the upper suspension liquid containing MoO_2 and Mo_2C coated carbon black particles and the Mo powder precipitated at the bottom (Fig. S2). Finally, the upper suspension liquid was evaporated at 80 °C for 24 h and the resultant powder was denoted by MoO_2–Mo_2C/C. For comparison, carbon black as conductive additive was mixed with commercial Mo_2C in a mass ratio of 1:4 to obtain a sample denoted by Mo_2C + C. The Pt/C (20 wt% Pt supported on Vulcan XC-72 carbon black) electrocatalyst was synthesized by a microwave-assisted polyol reduction method [29,30].

Material characterization

X-ray diffraction (XRD) was carried out to determine the crystalline structure of samples using a D/Max-2500pc

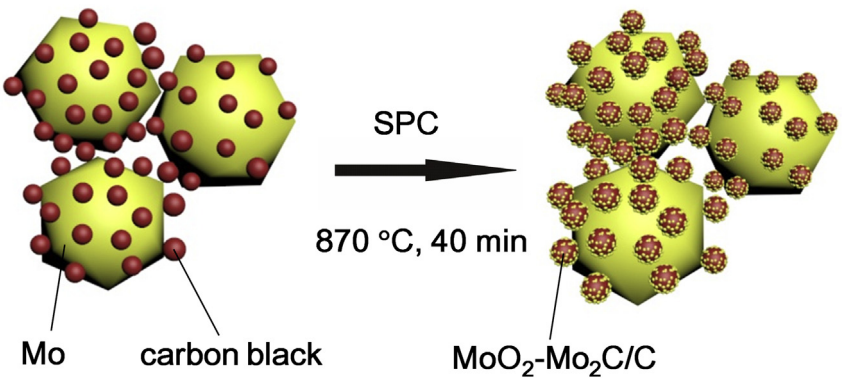


Fig. 1 – Schematic of preparation route of MoO_2–Mo_2C/C.

Please cite this article in press as: Zhang Y, et al., Molybdenum oxide and molybdenum carbide coated carbon black as an electrocatalyst for hydrogen evolution reaction in acidic media, International Journal of Hydrogen Energy (2017), https://doi.org/10.1016/j.ijhydene.2017.09.077